

Chem 51C Midterm Exam 2
101 points; 50 minutes
May 23, 2014

Answer
Key

Problem	Possible Points	Score
1	21	_____
2	12	_____
3	8	_____
4	18	_____
5	18	_____
6	24	_____
<hr/>		
Total	101	_____

Academic Honesty Policy. Academic honesty is strictly enforced on quizzes, exams, and other aspects of this course. Academic dishonesty will result in a failing grade in the class and a letter in the student's file. Activities constituting academic dishonesty include:

Cheating

- Copying from others during an examination.
- Communicating exam answers with other students during an examination.
- Offering another person's work as one's own.
- Taking an examination for another student or having someone take an examination for oneself.
- Tampering with an examination after it has been corrected, then returning it for more credit.
- Using unauthorized materials, prepared answers, written notes, or concealed information during an examination.

Dishonest Conduct

- Stealing or attempting to steal an examination or answer key from the instructor.
- Allowing another student to copy off of one's own work during a test.

Collusion

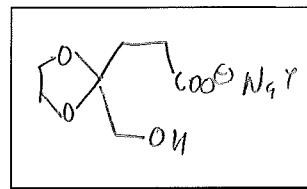
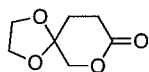
- Any student who knowingly or intentionally helps another student perform any of the above acts is subject to discipline for academic dishonesty.

I understand and will abide by this academic honesty policy: _____ (signature)

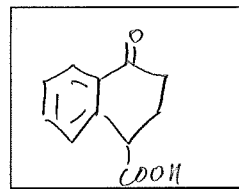
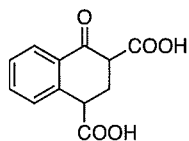
Seat: _____

1. Write the missing reactants, reagents, and products in the boxes. (3 points each, 21 points)

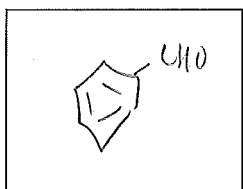
From
Smith
Prob.
22.52



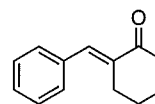
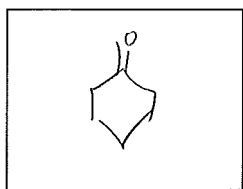
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Prob.
23.52b



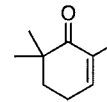
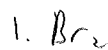
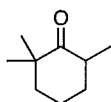
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24.7b



+

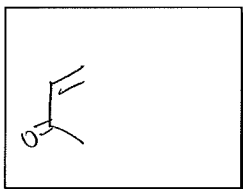


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Prob.
23.52f

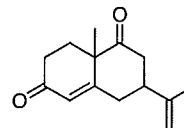
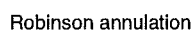
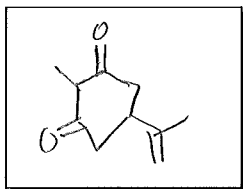


(for example
1. Br₂ / CH₂COH
2. K₂CO₃
(pyridine is used as
base in Stirling))

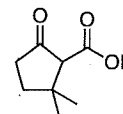
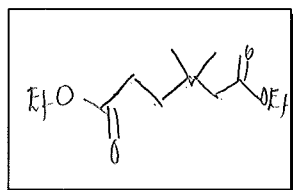
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Prob.
24.47a



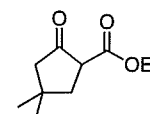
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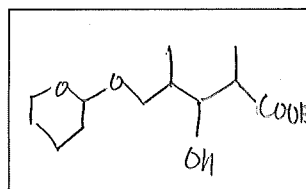
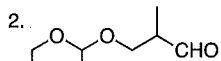
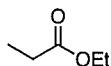
From
Smith
Prob.
24.20



+



From
Smith
Prob.
24.30b



2. (4 points each, 12 points)

a. Rank the following compounds in order of increasing reactivity in nucleophilic acyl substitution

(Smith Problem 22.42a): A < C < B

A. butanamide

B. butanoyl chloride

C. propyl butanoate

b. Rank the following compounds in order of increasing reactivity in nucleophilic acyl substitution

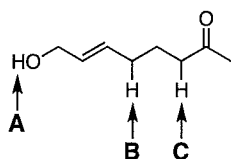
(Smith Problem 22.42b): C < A < B

A. $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$

B. $(\text{CF}_3\text{CO})_2\text{O}$

C. $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_3$

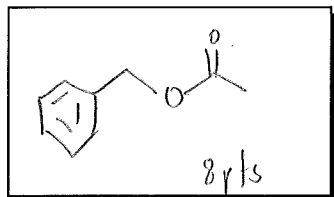
c. Rank the labeled protons in order of increasing acidity (Smith Problem 23.35c): B < C < A



3. A compound that is a major component of jasmine oil with a molecular formula of $\text{C}_9\text{H}_{10}\text{O}_2$ exhibits the following features in the IR and ^1H NMR spectrum. Write the structure of the compound in the box, below.
(Smith Problem 22.8, 8 points)

IR absorptions at 3091-2895 and 1743 cm^{-1}

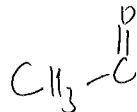
^1H NMR signals at 2.06 (singlet, 3 H), 5.08 (singlet 2 H), and 7.33 (broad singlet, 5 H) ppm



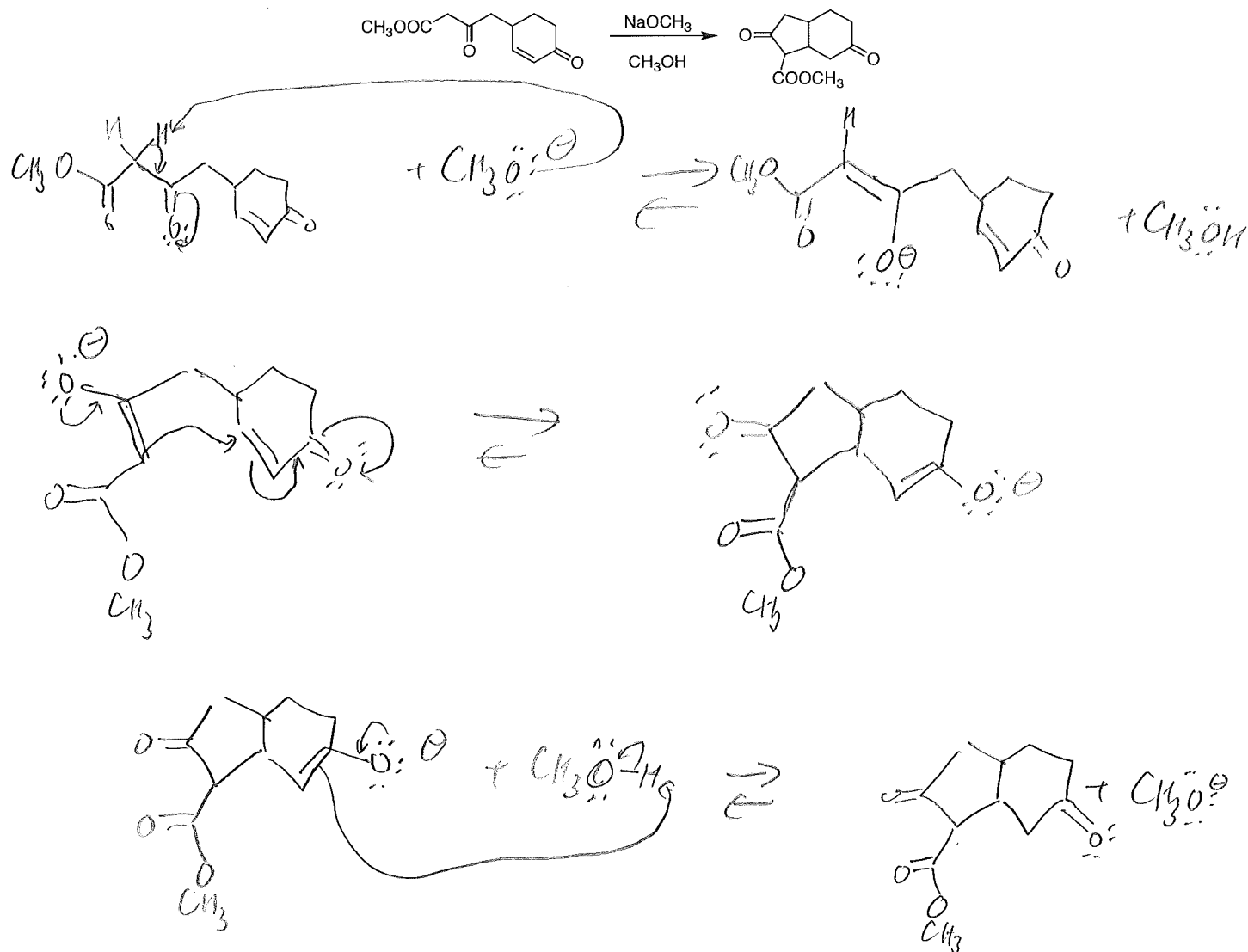
Some thoughts:

5 degrees unsaturation.

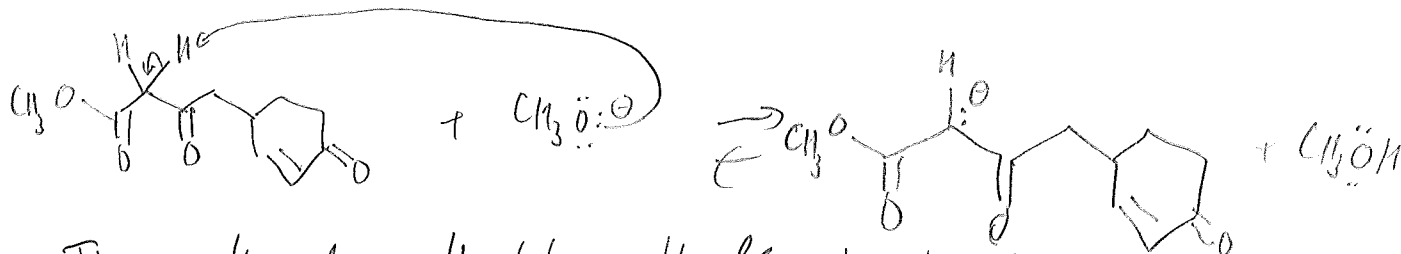
phenyl ring (C_6H_5) Carbonyl (ester)



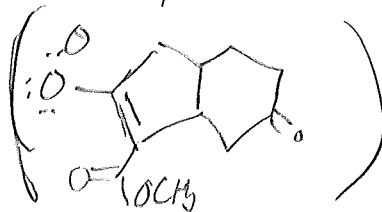
4. Draw a stepwise mechanism for the following cyclization reaction. (Adapted from Smith Problem 24.54, 18 points)



Notes: If you prefer to think about another resonance structure of the anion, that's OK, too:



The methoxide ultimately will deprotonate the product to give the enolate, which would then be protonated on workup with H_3O^+ , but we won't worry about either of these steps, as they go beyond the scope of the current problem.

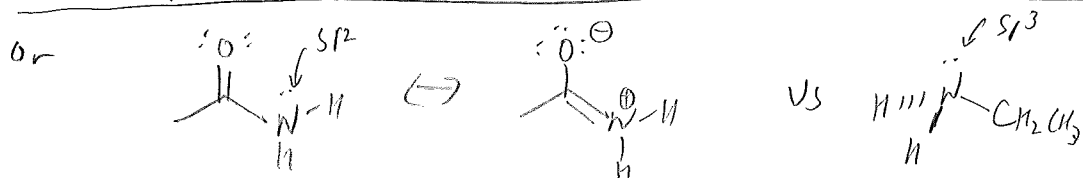


5. Provide concise explanations of the following. For most, a few words and a chemical equation or structures may suffice. Note that clarity counts and muddled answers containing irrelevancies will receive little or no credit.

Select three of the following four. (6 points each, 18 points total). Cross out the one that you do not wish to answer or only the first three problems will be graded.

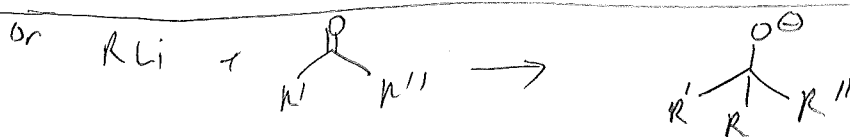
a. Explain why CH_3CONH_2 is a weaker base than $\text{CH}_3\text{CH}_2\text{NH}_2$ (Smith Problem 22.44)

The lone pair of electrons on nitrogen of the amide is tied up by resonance, so it is less basic than that of the amine.

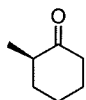


b. Organolithium reagents (RLi) are strong bases that can readily react with acidic protons. Explain why organolithium reagents are not used to generate enolates. (Smith problem 23.9)

Organolithium compounds add to carbonyl groups. Even though they are strongly basic, they are also strongly nucleophilic, and their reactions as nucleophiles dominate.

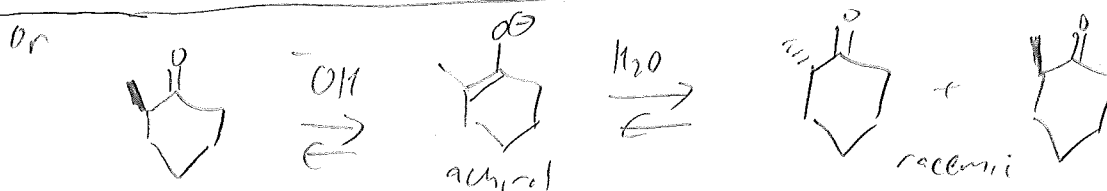


c. Explain why when (2R)-2-methylcyclohexanone is treated with NaOH in H_2O , the optically active solution gradually loses optical activity. (Smith Problem 23.11)

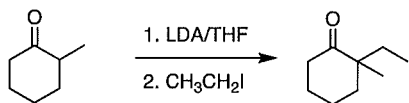


(2R)-2-methylcyclohexanone

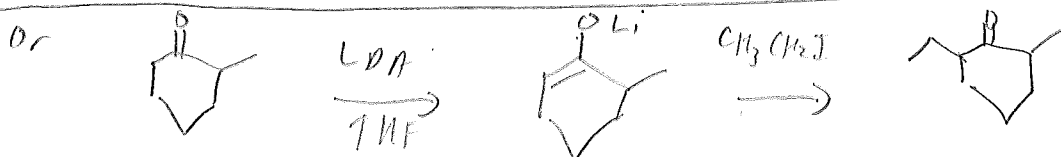
The enolate that forms reversibly is achiral



d. Explain why the following reaction will **not** proceed as written. (Smith Problem 23.57)

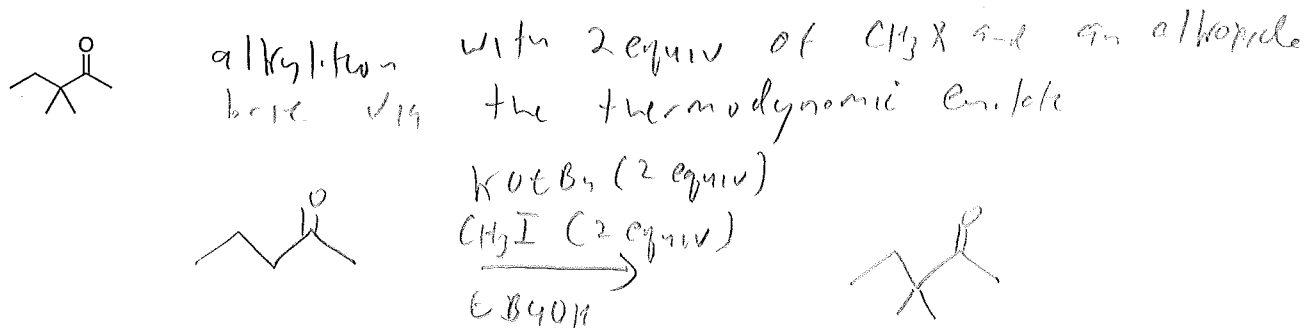


LDA removes the less sterically hindered proton to generate the wrong enolate.

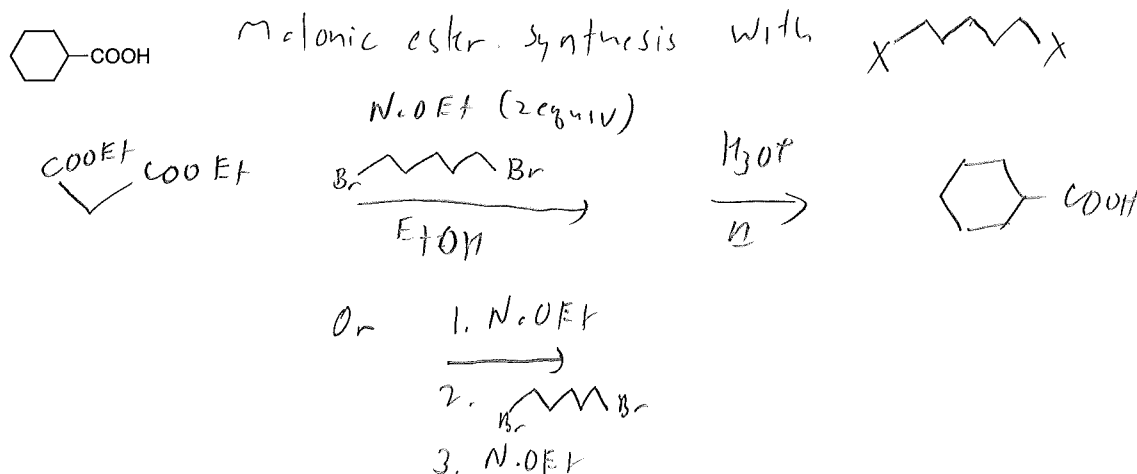


6. Select four of the following five. (6 points each, 24 points total). Cross out the one that you do not wish to answer or only the first four problems will be graded.

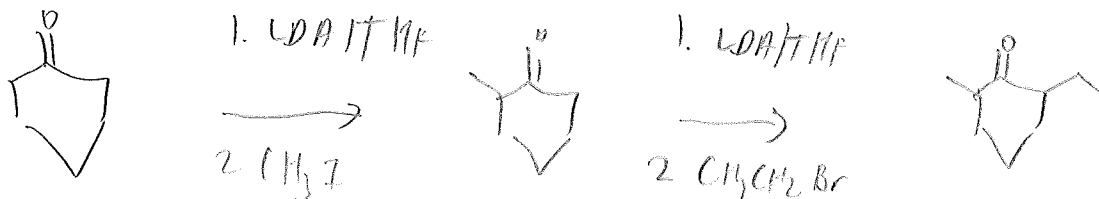
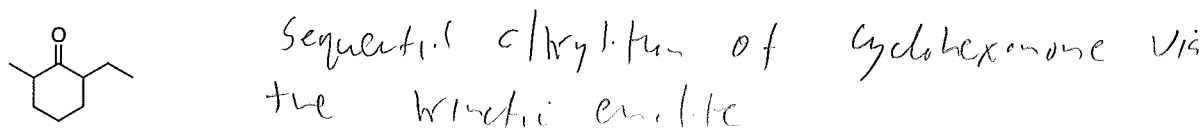
a. Synthesize the following compound from 2-pentanone and any other organic compounds that you need. You may use any organic or inorganic reagents that you require. (Adapted from Smith 23.19b)



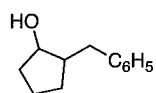
b. Synthesize the following compound from diethyl malonate and any other organic compounds that you need. You may use any organic or inorganic reagents that you require. (Adapted from Smith 23.48a)



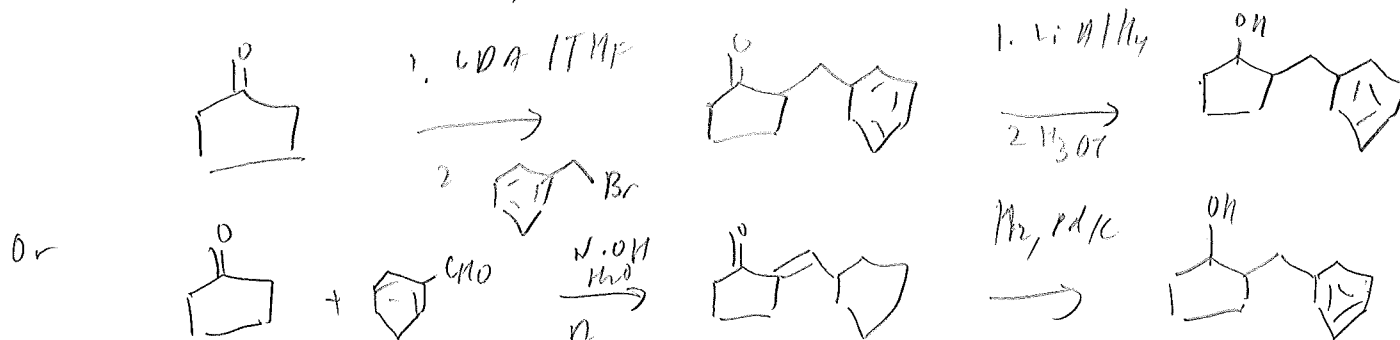
c. Devise a synthesis of the following compound from cyclohexanone and any other organic compounds that you need. You may use any organic or inorganic reagents that you require. (Adapted from Smith 23.66c)



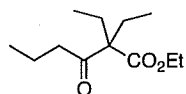
d. Devise a synthesis of the following compound from cyclopentanone and any other organic compounds that you need. You may use any organic or inorganic reagents that you require. (Adapted from Smith 24.63c)



Alkylation of cyclohexanone with a benzyl halide followed by reduction, for example:



e. Devise a synthesis of the following compound from CH₃CH₂CH₂CO₂Et and any other organic compounds that you need. You may use any organic or inorganic reagents that you require. (Adapted from Smith 24.64g)



Claisen condensation of ethyl butanoate followed by alkylation with an ethyl halide

